

# DETERMINATION OF MAJOR AND TRACE ELEMENTS IN CANADIAN SEDIMENT REFERENCE SAMPLES USING PORTABLE ENERGY-DISPERSIVE X-RAY FLUORESCENCE (ED-XRF) SPECTROMETER AND IMPLICATIONS FOR GEOCHEMICAL SURVEYS

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for calibration of the portable ED-XRF spectrometer

CCRMP-CANMET Reference Material

Figure 6. The ED-XRF results compared with the published values for the Canadian sediment reference samples (Lynch, 1990, 1996, 1999).



Energy, Mines

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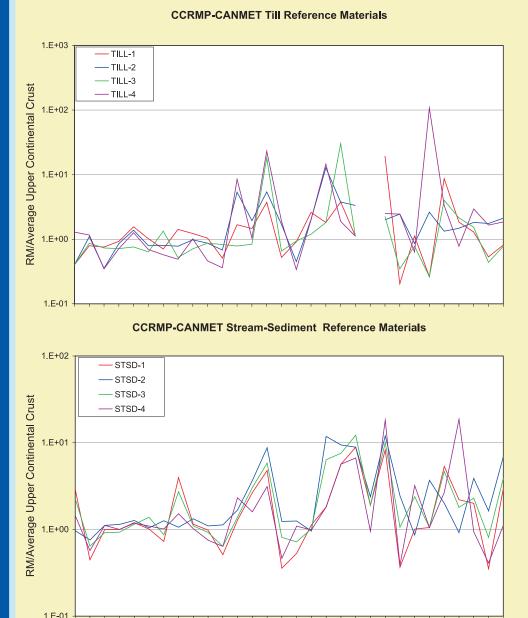
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For More Information:

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#### INTRODUCTION

Regional geochemical surveys are an important part of geoscience studies in both mineral exploration and environmental monitoring. A till or stream/lake sediment survey can consist of collecting several thousand samples and chemical analysis for more than 50 elements (e.g., Lett et al., 2008). Sediment samples are usually analyzed using aqua regia-atomic absorption spectrophotometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) and instrumental neutron activation analysis

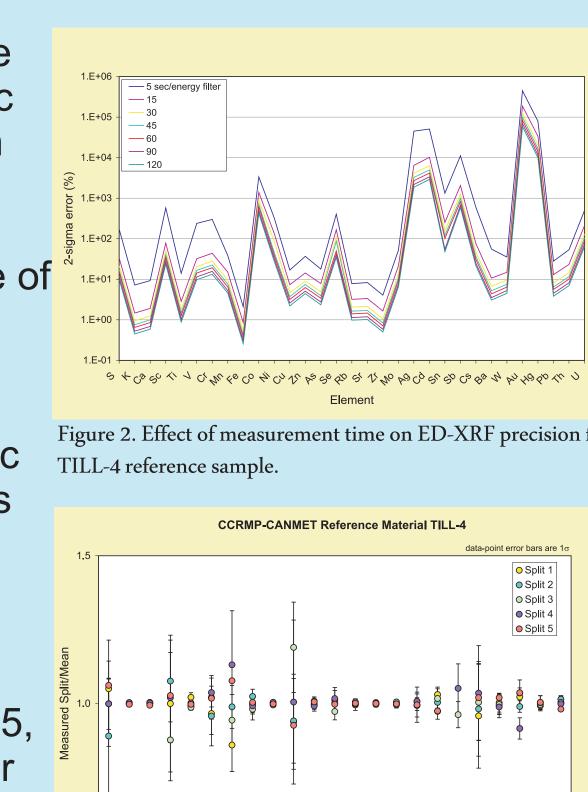


The energy dispersive X-ray fluorescence (ED-XRF) spectrometry is capable of simultaneous, multielemental, non-destructive analysis in a wide dynamic concentration range from 100% to ppm levels with excellent accuracy and precision (e.g., Piorek, 1994). Recent advances in the ED-XRF technology have made it field portable and effective technique for geochemical surveys (e.g., Weindorf et al., 2012). In this study, a portable ED-XRF spectrometer was used to analyze 24 elements (S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Sn, Cs, Ba, W, Pb, Th, U) in four till, four stream-sediment, and four lake-sediment samples from the Canadian Certified Reference Materials Project (CCRMP-CANMET) (Fig. 1). These reference samples have been widely used as primary-control standards in geochemical surveys because of their homogeneity, particle size (<74 µm) and concentration gradient for a large number of elements within each sample type. The results of this study are compared with the published "provisional values" using total extraction analytical techniques in a number of laboratories (Lynch, 1990, 1996, 1999). The goal of this study is to evaluate the usefulness of the portable ED-XRF technique for negional geochemical surveys.

#### EXPERIMENTAL

All measurements were carried out on 8 mm sample spot with air in the X-ray path on a Thermo Scientific Niton FXL 950 ED-XRF spectrometer equipped with 50 kV, 200 μA, 4W silver X-ray tube and a high resolution silicon drift detector. Average detector resolution was  $155 \pm 3 \text{ eV}$  ( $1\sigma$ , n = 15) in the course of this study (January 14-18, 2013). For each sample, 15- to 20-g splits of the powdered sample were packed in a plastic cup with a bottom made of ultrathin (4 µm) polypropylene film held by two concentric plastic rings. Compton scatter radiation was used as an internal standard to compensate for variations in sample matrix, particle size, packing density, and instrumental operating conditions (e.g., Nielson, 1979). To monitor internal precision as a function of 15, 30, 45, 60, 90, and 120 seconds per energy filter (Fig. 2). The total measurement time of 180 seconds (60 seconds per filter) provided acceptable counting statistics for all analyzed elements. Each sample was

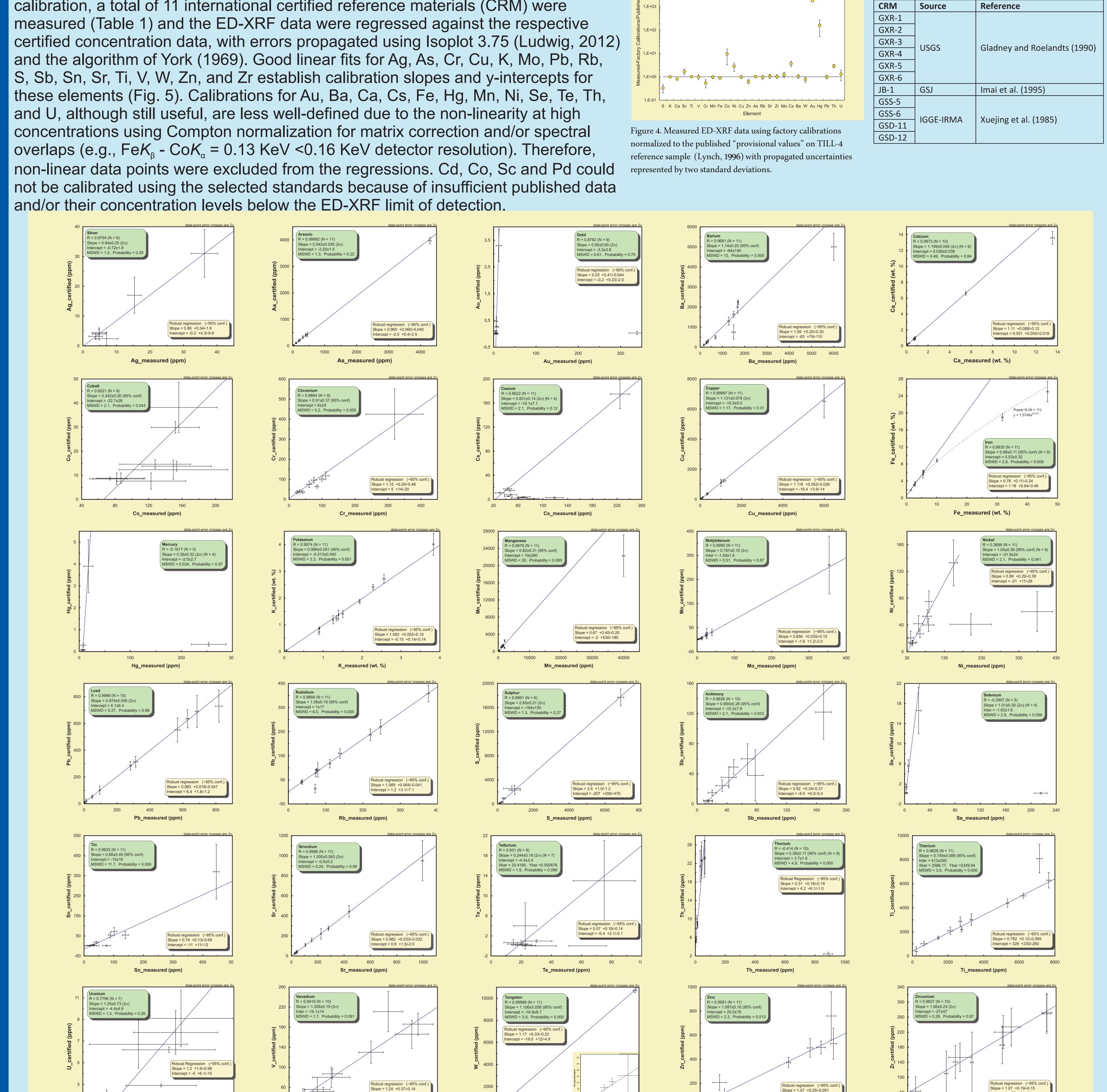
Figure 3. Average results on each duplicate split of TILL-4 consecutive runs. Average of all results per sample was used, with the within-cup reproducibility reflected in the standard deviation. In addition, five samples of TILL-4 reference material were prepared and analyzed to estimate the inter-sample reproducibility. The similar within- and inter-sample means and the standard deviations indicate that the sample preparation does not contribute error beyond the counting statistics



# **ED-XRF CALIBRATION**

ED-XRF data on TILL-4 using factory calibration indicate significant bias relative to the published values (Lynch, 1996) for some elements (Fig. 4). To improve the measured (Table 1) and the ED-XRF data were regressed against the respective and the algorithm of York (1969). Good linear fits for Ag, As, Cr, Cu, K, Mo, Pb, Rb, S, Sb, Sn, Sr, Ti, V, W, Zn, and Zr establish calibration slopes and y-intercepts for these elements (Fig. 5). Calibrations for Au, Ba, Ca, Cs, Fe, Hg, Mn, Ni, Se, Te, Th, and U, although still useful, are less well-defined due to the non-linearity at high concentrations using Compton normalization for matrix correction and/or spectral overlaps (e.g., Fe $K_{g}$  - Co $K_{g}$  = 0.13 KeV < 0.16 KeV detector resolution). Therefore, non-linear data points were excluded from the regressions. Cd, Co, Sc and Pd could not be calibrated using the selected standards because of insufficient published data

30 50 70 90 110 130 150 170



W\_measured (ppm)

Figure 5. X-Y error-weighted, least-squares regressions of ED-XRF data against certified values for international standards showing calibration slopes and y-intercepts with propagated 2-sigma/95% conf. errors. MSWD = Mean Square of Weighted Deviates (York, 1969).

# RESULTS AND DISCUSSION

The results for the 12 Canadian sediment reference samples are plotted together with the published the uncertainties represented by two standard deviations among 5 replicate analyses of each sample except TILL-4 (n = 25). The ED-XRF results are consistent with the published data within the uncertainties for V, Cr, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, W and Pb in all or most of the reference samples. In addition, S and Ca show good agreement with the published values below 0.2% and 3% concentration levels, respectively, and the magnitude of deviation from the "true" value for both elements, along with K and Ba, is strongly correlated with Loss-on-Ignition (LOI, up to 44%) in these samples (Fig. 7). This indicates that high LOI contents (mainly H<sub>2</sub>O) in these samples impact accuracy of S, Ca, K and Ba determinations by the portable ED-XRF. Other elements that show some correlation with LOI are Cu, Zr, and Mo (not shown in Fig. 7 for clarity). All Ti, Mn and Fe data have a small but significant systematic error, whereas Cs, Ba, Th and U concentrations, although accurate in some samples, perhaps reflect spectral peak overlaps in others. Therefore, anomalous concentrations of these elements in unknown samples should be treated with caution. In addition, Se (2.7 ppm) and Sn (10 ppm) were detected in TILL-4. Precision (2σ) is better than 6% (average 1.6%) at a concentration level of 30 ppm or greater for most of the trace elements except Cs; larger relative errors are associated with low concentrations Although detected in some of the calibration standards, concentrations of Co, Ag, Cd, Sb, Au, and Hg in the Canadian sediment reference samples were all below the detection limits of the portable ED-XRF.



CCRMP-CANMET Reference Material

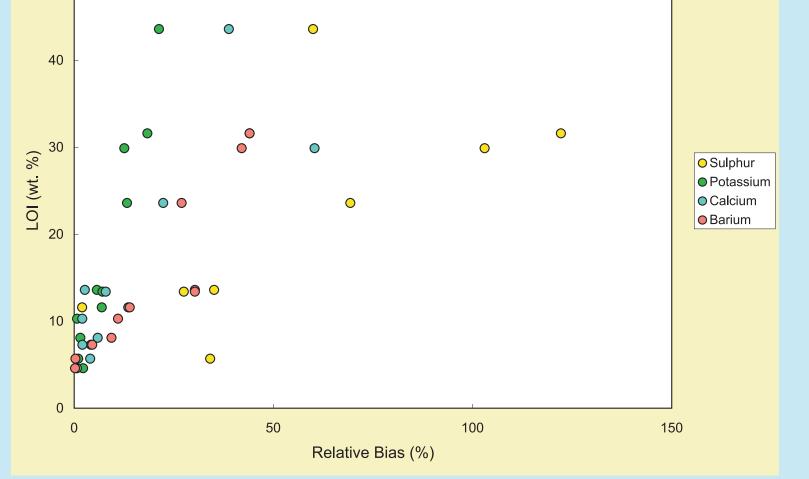


Figure 7. Plot of relative bias for S, K, Ca, and Ba concentrations by ED-XRF spectrometry versus Loss-on-Ignition (LOI, wt. %) in the Canadian sediment reference samples showing correlations between the LOI (mainly H,O in these samples) and the magnitude of deviation of the ED-XRF data from the published values (Lynch, 1990, 1996). Relative Bias (%) = 100\*(abs(Measured Concentration)

# CONCLUSIONS

Good agreement of the ED-XRF data for base metals, arsenic, rubidium, strontium, and zirconium, with the published values in the reference sediment samples shows that the portable ED-XRF spectrometer can be successfully used, with Compton scatter normalization for matrix correction, for the precise and accurate analysis of till, stream- or lake-sediment samples in mineral exploration, geochemical mapping and environmental monitoring. The technique is also fast, non-destructive, and less time-consuming in sample preparation compared with other analytical methods.

# **FUTURE WORK**

 Develop spectral overlap corrections using Compton scatter radiation normalization algorithm.

◆Fine-tune calibrations for Ti, Mn, Fe.

◆Calibrate Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, Y, Nb, La, Ce, Pr, Nd, Hf, Ta, Re and Bi determined using a different ED-XRF algorithm that has a high dynamic concentration range from 100% to ppm

#### ACKNOWLEDGEMENTS

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